



Electrical and optical investigations in Te–Ge–Ag and Te–Ge–AgI chalcogenide glasses

S. Cui, David Le Coq, C. Boussard-Plédel, B. Bureau

► To cite this version:

S. Cui, David Le Coq, C. Boussard-Plédel, B. Bureau. Electrical and optical investigations in Te–Ge–Ag and Te–Ge–AgI chalcogenide glasses. *Journal of Alloys and Compounds*, 2015, 639, pp.173-179. 10.1016/j.jallcom.2015.03.138 . hal-01139764

HAL Id: hal-01139764

<https://hal.science/hal-01139764>

Submitted on 4 Nov 2015

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Electrical and optical investigations in Te-Ge-Ag and Te-Ge-AgI chalcogenide glasses

S. Cui^{a,b}, D. Le Coq^{a,*}, C. Boussard-Plédel^a, B. Bureau^a

(a) Glass and Ceramic Laboratory, Institute of Chemical Sciences of Rennes, UMR-CNRS6226, University of Rennes 1, 35042 Rennes cedex, France

(b) Department of Materials Science and Engineering, Zhejiang University, 38 Zheda Road, Hangzhou, 310027, China

(*) Corresponding author: david.lecoq@univ-rennes1.fr

Tel/Fax: +33 (0)2 23235423 / 5611

Abstract

(GeTe₄)_{100-x}Ag_x and (GeTe₄)_{100-x}(AgI)_x glasses were prepared by a melting-quenching method. The glass electrical conductivity was investigated by both electrochemical impedance spectroscopy at different temperatures from 283K to 333K and four-probe method at room temperature (293K). Meanwhile, as a major factor determining the electrical conductivity of a solid, optical band gap was also studied. By comparing the electrical conductivity values and glass optical band gap evolution, it was found that (GeTe₄)_{100-x}Ag_x glasses are mainly electronic conductive. On the other hand, the electrical conductivities of (GeTe₄)_{100-x}(AgI)_x glasses firstly show a monotonic decrease by increasing AgI up to 15 mol. %, and then an increase when the AgI content is higher than 15 mol. %. The activation energy E_a and the pre-exponential factor σ_0 show apparent turning point when AgI content is 15 mol. %, signifying a conductivity mechanism change. In this paper, correlations between the conductivity and hypothetical structures in (GeTe₄)_{100-x}Ag_x and (GeTe₄)_{100-x}(AgI)_x glasses are done and the importance of the Ag role is underlined.

Keywords : chalcogenide glasses; electrical conductivity; impedance spectroscopy;

1. Introduction

Tellurium glasses are matchless materials for mid and far infrared applications. Nevertheless, they are also unstable against crystallization and shaping such glasses is a challenging operation. Recently, some new compositions in the system $(\text{GeTe}_4)_{100-x}(\text{AgI})_x$ have been prepared and optical fibers were fabricated and used for sensing until $16\mu\text{m}$ [1, 2]. A structural study has also been carried out to try to better understand the unique stability of these materials. On the other hand, chalcogenide glasses, especially tellurium glasses, have attracted considerable attention in recent years due to their electrical properties [3-14]. Moreover, the chalcogenide glasses containing metal cations are able to behave as fast ionic conductors [7, 15], showing their potential application as solid electrolytes in the solid-state batteries, fuel cell technologies, and other electrochemical devices [16-19]. Among them, a variety of silver-containing chalcogenide glasses with high ionic conductivity has been explored [6, 9, 11, 15, 19-22]. In particular, silver halide doped glasses show very high ionic conductivity [11, 15, 19-21, 23]. It has been proved that ionic conductivity of chalcogenide glasses can be enhanced by several orders of magnitude upon increasing the concentration of silver iodide with relatively small and polarizable cations [20, 21]. Indeed, AgI is a well-known ion conductor compound [24] and at temperatures above 420 K, it exhibits a phase transition from β phase to α phase. This high-temperature phase has an ionic conductivity similar to that of its liquid phase. Up to now, the chalcogenide glass ionic conductivity studies are mainly focused on sulfur and selenium-based glasses. In contrast, Te-based glasses, due to their narrow band gap and low thermal stability, are often used as memory devices based on thermally driven amorphous crystalline phase changes [25, 26]. Very little is known about the ion transport properties in telluride glasses if we except a few papers [10, 27-30]. In that context, it appeared interesting to lead a study on the electrical conductivities (electronic versus ionic) on these $(\text{GeTe}_4)_{100-x}(\text{AgI})_x$ glasses in order to get valuable information on their structure. Note that both Ag and AgI doped sulfide and selenide glasses are ionic conductive [9, 15, 30, 31], whereas for telluride equivalent systems there is a competition between ionic and electronic conductivities [10]. So, in the present contribution, the electrical property of $(\text{GeTe}_4)_{100-x}\text{Ag}_x$ glasses will be investigated together with the $(\text{GeTe}_4)_{100-x}(\text{AgI})_x$ system by electrochemical impedance spectroscopy and four probe method. Near infrared transmittance spectrum will be also collected in order to compare optical and electronic band gap.

2. Experiments

(GeTe₄)_{100-x}Ag_x (x=0, 5, 10, 15, and 20) glasses (named as TG-Ag0, TG-Ag5, TG-Ag10, TG-Ag15, and TG-Ag20 respectively) and (GeTe₄)_{100-x}(AgI)_x (x=0, 5, 10, 12.5, 15, 17.5, 20, and 25) glasses (named as TG-AgI0, TG-AgI5, TG-AgI10, TG-AgI12.5, TG-AgI15, TG-AgI17.5, TG-AgI20, TG-AgI25) were prepared by melt-quenching method.

Appropriate amounts of high purity (5N) raw materials Te, Ge mixed with Ag or AgI were sealed in evacuated ($\sim 10^{-3}$ Pa) silica tubes (OD = 9 mm and ID = 7 mm) and melted in a rocking furnace at 750°C for 10 hours. Then, the glasses were quenched in water and annealed at a temperature 5°C lower than glass transition temperature T_g for 3 hours to relieve internal stresses. The samples of 10 g were cut and optical polished into discs with a diameter of 7 mm and a thickness of 1 mm for all experiments. The glass homogeneity was checked by Energy-dispersive X-ray spectroscopy and X-ray Diffraction. The AC electrical conductivity was calculated from impedance measurements carried out using a TSC SW_c measuring cell in combination with a Microcell HC set-up (Rhd instruments). Samples were coated with gold on each face and placed in between two mirror-like polished stainless disc electrodes. To ensure a good electrical contact, a contact pressure of approximately 80 kPa was applied. All measurements were performed using Autolab workstation (PGSTAT302N with FRA32M and ECD module) from 283K up to 333K with a frequency range from 800 kHz down to 1 Hz. Beforehand, DC electrical conductivity was also carried out on the same samples at room temperature by a S-302 four point probe system from Lucas Labs. The transmittance spectra between 1 and 2.5 μm (1.240-0.496 eV) were measured using a Perkin-Elmer Lambda 950 UV-VIS-NIR spectrophotometer. Spectra above 2.5 μm (<0.496 eV) were recorded by a Bruker Vector 27 FT-IR Spectrometer equipped with a DTGS detector.

3. Results

3.1 DC electrical conductivity measured by four probe system

Fig. 1 depicts the DC electrical conductivities σ_{DC} of (GeTe₄)_{100-x}Ag_x and (GeTe₄)_{100-x}(AgI)_x glasses measured by four probe system at room temperature (293K). For comparison, the conductivities of (GeTe₄)_{100-x}I_x (x=0, 5, and 14) glasses prepared by melt quenching technique are also given.

For $(\text{GeTe}_4)_{100-x}\text{Ag}_x$ glasses, a monotonic increase of the DC conductivity from $6.37 \times 10^{-6} \text{ S}\cdot\text{cm}^{-1}$ up to $9.22 \times 10^{-5} \text{ S}\cdot\text{cm}^{-1}$ is observed when the molar content of Ag is increased from 0% up to 20% (Table 1). At contrary, the DC conductivity of $(\text{GeTe}_4)_{100-x}\text{I}_x$ and $(\text{GeTe}_4)_{100-x}(\text{AgI})_x$ glasses exhibits a decrease when the content of AgI and I is growing up to 15 mol. %. For I-based glasses, the linear decrease is relatively weak since the value of the $(\text{GeTe}_4)_{86}\text{I}_{14}$ conductivity only decreases down to $1.84 \times 10^{-6} \text{ S}\cdot\text{cm}^{-1}$. However, for AgI-based glasses, the decrease is more pronounced since it is close to $2.67 \times 10^{-7} \text{ S}\cdot\text{cm}^{-1}$ for $(\text{GeTe}_4)_{85}(\text{AgI})_{15}$. It is also interesting to note that when the AgI molar content is beyond 15%, electrical conductivity cannot be measured by four probe method anymore, although glasses with up to 25 mol. % of AgI were synthesized. Another point is interesting to highlight at this level: the decrease of conductivity is more evident in AgI-based glasses. As a matter of fact, the addition of Ag and I alone shows a positive and a negative effect on the conductivity, respectively. Consequently, by adding the two elements together, like in AgI-based glasses, the expected conductivity behavior should be intermediate, whereas a more important decrease of the conductivity is observed.

3.2 AC electrical conductivity by impedance spectroscopy

The impedance spectroscopy measurements are operated in AC mode, indicating that no phenomenon of blocking electrode occurs whatever the charge carriers. The AC electrical conductivity of both $(\text{GeTe}_4)_{100-x}\text{Ag}_x$ and $(\text{GeTe}_4)_{100-x}(\text{AgI})_x$ glasses have been measured, including glasses with AgI beyond 15% (Fig. 2 and Table 1). $(\text{GeTe}_4)_{100-x}\text{I}_x$ glasses, due to the intrinsic volatility of iodine, are quite unstable, and their compositions are difficult to accurately control. Thus, their conductivity using impedance spectroscopy was not measured. As an example, Fig. 2a shows typical Nyquist's plot coming from impedance measurements. In the present case, the TG-AgI20 glass is investigated at temperatures between 283K and 333K. $Z'(\omega)$ and $Z''(\omega)$ are the real and the imaginary parts of the impedance. The sample resistance R_s was determined by extrapolating the semicircle to the $Z'(\omega)$ axis at low frequencies. Then, the AC conductivity σ_{AC} values at different temperatures can be calculated according to,

$$\sigma_{AC} = \frac{t}{A \cdot R_s} \quad (1)$$

Where A is the surface area and t is the sample thickness.

In Fig. 2a, it is also observed that as expected the resistance of the glass sample is decreasing following the temperature meaning that the conductivity is increased. This is quite usual with both ionic conductors and electronic (or hole) semiconductors [9, 30] because the two conduction processes are thermally activated processes usually visualized as jumping over energy barriers.

In fact, the temperature dependence of the AC conductivity σ_{AC} should obey an Arrhenius law,

$$\sigma_{AC} = \frac{\sigma_0}{T} \exp \left(-\frac{E_a}{kT} \right) \quad (2)$$

where σ_0 is the pre-exponential factor, E_a is the activation energy, k is the Boltzmann constant, and T is the temperature. The σ_{AC} evolution of both $(\text{GeTe}_4)_{100-x}(\text{AgI})_x$ and $(\text{GeTe}_4)_{100-x}\text{Ag}_x$ glasses are also shown in Figs. 2b, 2c, and 2d as a function of the reverse temperature. Clearly, the data obey reasonably well Arrhenius law in the measuring temperature range.

3.3 Optical band gap evolution

Note that the band gap is a major factor determining the electronic (or hole) conductivity of a semiconductor. To explain this electrical conductivity increase, optical band gap E_{opt} should be investigated. In this work, the absorption coefficients (Fig. 3) are obtained by converting transmittance using,

$$\alpha = -\frac{\ln T}{t} \quad (3)$$

where T and t represent transmittance and bulk thickness respectively. The wavelength corresponding to E_{opt} is then determined using the suitable Tauc equation for indirect semiconductors [32].

For $(\text{GeTe}_4)_{100-x}\text{Ag}_x$ glasses, by adding Ag, E_{opt} was firstly decreased from 0.645 eV ($x = 0$) down to 0.573 eV ($x = 15$) and then remains constant (Table 1). On the contrary, by adding AgI, the $(\text{GeTe}_4)_{100-x}(\text{AgI})_x$ glasses show a continuous E_{opt} increase from 0.645 eV ($x=0$) until 0.915 eV ($x=25$).

4. Discussion

As a semiconductor, the charge carrier (electrons or holes) concentrations of Te-based chalcogenide glass are greatly dependent on the band gap. In Fig. 3, the observed decrease of the optical band gap with the increase of Ag concentration was attributed to the structural transformation. Actually, Ag enters the glass structure and forms its own connected structure [33]. In this constrained network structure, Ag may cause an increase in disorder and induce energy levels in the band gap. Due to the high doping concentration, the density of states of these dopants increases and forms a continuum of states just like in the bands and effectively decreases the band gap. This behavior contributes to the migration of photo-generated electrons. As a result, more electrons can go to conduction band, generating a higher conductivity. When Ag content is beyond 15%, the intermediate levels in the band gap are fully occupied and the glass becomes more metallic. Thus, the glass optical band gap stops decreasing. Nevertheless, the electrons of Ag still enter into the glass network continuously, generating a higher conductivity.

On the contrary, the increase of AgI content can broaden E_{opt} of $(\text{GeTe}_4)_{100-x}(\text{AgI})_x$ glasses. Indeed, the influence of Ag and I on E_{opt} of glass is totally opposite. Clearly, in $(\text{GeTe}_4)_{100-x}(\text{AgI})_x$ glasses, iodine plays a benefit role to trap the electronic charges, enlarging E_{opt} , and the effect of iodine supersedes that of silver. In both Fig. 1 and Fig. 2c, it can be clearly seen that by adding AgI ($x \leq 15$), glasses show a continuous decrease of electrical conductivity. According to energy band theory, the electronic conductivity should keep decreasing when AgI content is above 15%. However, Fig. 2d shows that the total conductivity increases with AgI addition ($x \geq 15$), which is not consistent with the optical band gap evolution, assuming the generation of a new type of charge carrier.

In Fig. 4, one observes that the electrical conductivities obtained by both methods have the same order of magnitude, which confirms their reliabilities. In $(\text{GeTe}_4)_{100-x}(\text{AgI})_x$ glasses, when AgI is less than 15%, the electrical conductivity shows a monotonic decrease by adding AgI and reached to the minimum when AgI is 15%. However, when AgI is more than 15%, the glass conductivity measured by impedance spectroscopy starts to increase and the rising rate is higher than the previous decreasing rate. Iodine, as an electronegative element, plays a benefit role to trap the electronic charges and acts as a kind of electron absorber in chalcogenide glasses [34, 35]. On the basis of the continuous electron decrease caused by AgI, this σ transition trend can

be only explained by the appearance of novel charge carriers: ions. Indeed, from the impedance spectroscopy (Fig. 2a) of TG-AgI20 glass, it can be observed that at low frequency region, the beginning of a polarization arm appears and turns away gradually from the $Z'(\omega)$ axis. The occurrence of this polarization arm indicates a diffusion-controlled process[36]. In this low frequency region, the diffusion of active species can generate a charge accumulation on the sample-electrode interface during potential oscillation. This is a typical feature of ion conductance. As a result, a transition of $(\text{GeTe}_4)_{100-x}(\text{AgI})_x$ glasses from electronic to ionic conductors by increasing AgI content is predicted. This could also explain the blocking of σ_{DC} measurement when AgI is higher than 15%.

To have a clear view of this charge carrier evolution, the impedance spectroscopy of $(\text{GeTe}_4)_{100-x}(\text{AgI})_x$ glasses at 283 K were compared in Fig. 5. The onsets of Fig. 5 highlight the data of TG-AgI15, TG-AgI20, and TG-AgI25 glasses at low frequencies. It is clear that the ionic conductivity starts to appear when AgI content is more than 15% since the polarization arms become more pronounced, signifying an increase of ion diffusion. This behavior has already been observed for As_2Te_3 -AgI glasses but with a threshold in AgI molar concentration close to 50% [29] that is relatively high compared of the 15% observed here. For comparison, the electrochemical impedances of $(\text{GeTe}_4)_{100-x}\text{Ag}_x$ glasses were also measured at different temperatures. None spectrum reveals a polarization arm, which is consistent with a predominance of an electronic-type conductivity. Thus, $(\text{GeTe}_4)_{100-x}\text{Ag}_x$ glasses, similar to $(\text{As}_{40}\text{Te}_{60})_{100-x}\text{Ag}_x$ glasses[37, 38], exhibit an electronic nature.

According to previous results (Figs. 2b, c and d), the electrical conductivity values obey reasonably well Arrhenius law in the measuring temperature range. By exponential fitting, the activation energy E_a and pre-exponential factor σ_0 were obtained and listed in Table 1. The Arrhenius Activation energy term from the Arrhenius equation can be regarded as a parameter that indicates the sensitivity of the reaction rate to temperature. For $(\text{GeTe}_4)_{100-x}(\text{AgI})_x$ glasses, if the transition from electronic ($\text{AgI} \leq 15\%$) to ionic conduction ($\text{AgI} \geq 15\%$) occurs as assumed by the previous analyses, it can be predicted that E_a at lower AgI content should increase due to the decrease of the electronic conduction. Then, for the higher AgI rate, E_a should decrease because of the concentration increase of ions as charge carriers. For the $(\text{GeTe}_4)_{100-x}\text{Ag}_x$ glasses,

the electronic conductivity monotonically increases with the Ag rate and so, E_a is expected to decrease. Actually, all the analysis mentioned above were confirmed as observed in Fig. 6a.

On the other hand, the theoretical significance of the pre-exponential term σ_0 in the Arrhenius conductivity equation is difficult to interpret. Some authors have reported that σ_0 is proportional to the amount of mobile charges [9, 39], whereas others have stated that σ_0 is composition independent [6, 40-43]. In our case, the conductivity mechanism of $(\text{GeTe}_4)_{100-x}\text{Ag}_x$ glasses is unchanged, and σ_0 does not change significantly with the composition as exhibited in Fig. 6. For $(\text{GeTe}_4)_{100-x}(\text{AgI})_x$ glasses, σ_0 shows an obvious inflection point when AgI molar content is 15%, which can be also probably be correlated to the charge carriers or conduction mechanism change.

Recently, the GeTe_4 -AgI glass structures have also been studied by X-ray and extended-X-ray absorption spectroscopy using reverse Monte Carlo method [44]. It appeared that the Ag is surrounded by about three neighbors, rather Te for $x=15\%$, and a mixture of Te and I for $x=25\%$. The Fig. 1 shows that conductivity increases with the Ag addition and decreases with I addition. Naturally, addition of both Ag and I is expected to show an intermediate feature. But, it is clearly shown in Fig. 1 that the addition of AgI decreases more quickly the conductivity. We assume that the role played by iodine is the same whatever the I-based or AgI-based glasses. So, it seems that the structural role played by Ag is different in these glass families. Thus, we rather assume covalent type bonds for Ag in the GeTe_4 -Ag system and ionic bond type of Ag^+ with Te and I for the GeTe_4 -AgI system. This hypothesis is also based on the fact that whatever the Ag content in $(\text{GeTe}_4)_{100-x}\text{Ag}_x$ no polarization arm has been observed, even if the frequency measurement is dropped down to 0.01 mHz. Figs. 7a and 7b propose a schematic representation of these two situations.

As far as iodine is concerned, iodine atom acts as glass network terminator in chalcogenide glass [11, 45, 46]. In telluride glass [44, 47], iodine also acts as an electron getter and tend to prevent Te from crystallizing. Very recently, it has been shown that iodine is rather connected to Ge and therefore opens up the network by generating larger rings without breaking the continuity of the structure [47]. Indeed, it cut the vitreous skeleton, meaning that the glass structure becomes more flexible. When AgI content is beyond 15%, the glass structure is sufficiently opened up by iodine and some channels of diffusion appear for Ag^+ . Consequently, the ionic

conductivity becomes more and more predominant and so, the structural description is in good agreement with the sharp increase of the ionic conductivity.

The $(\text{GeTe}_4)_{100-x}(\text{AgI})_x$ glasses have been developed for designing sensors working in the far infrared range, especially as optical fibers [1, 2]. To avoid crystallization during fiber drawing process, a good thermal stability is needed. The results displayed in this study help to understand the reasons why these glasses show such interesting properties. The strong localization of the electrons caused by Ag-Te and Ge-I bonds allows to explain why the $(\text{GeTe}_4)_{100-x}(\text{AgI})_x$ glasses possess a lower free electron concentration than tellurium glasses without AgI. Indeed, in this glass series, the compositions from TG-AgI10 to TG-AgI20 do not show any crystallization peak by thermal analysis, meaning that the simultaneous introduction of Ag and I in GeTe_4 -based glass plays a beneficial role on the glass thermal stability [2, 46]. In addition, as a low band-gap amorphous semiconductor, the attenuation of Te-based glass fiber is shown to strongly depend on extrinsic impurity but also on intrinsic charge carrier populations [48]. Thus, a low free electron rate in $(\text{GeTe}_4)_{100-x}(\text{AgI})_x$ glasses is beneficial to decrease fiber optical losses. Meanwhile, ionic conductivity should also be avoided. Thus, as experimentally demonstrated the TG-AgI15 composition appears to be the best candidate to draw optical fiber for infrared sensing.

5. Conclusion

By adding Ag, the $(\text{GeTe}_4)_{100-x}\text{Ag}_x$ glasses always exhibit an electronic-type conductivity that monotonously increases. In contrast, the $(\text{GeTe}_4)_{100-x}(\text{AgI})_x$ glasses show a total conductivity that first declined and then increased during the increase of AgI content. This was assigned to a transition from electronic to ionic conductors that occurs for AgI concentration equal to 15%. The activation energy and the pre-exponential factor also show a change of behavior around 15% mol. that is quite consistent with a change of majority conductivity type (electronic vs ionic).

By comparison of the electrical properties of $(\text{GeTe}_4)_{100-x}\text{Ag}_x$ and $(\text{GeTe}_4)_{100-x}(\text{AgI})_x$ glasses it is underlined that Ag could play a key-role in the structure. In the Ag-based system, silver is assumed to be a glass former. In AgI- based system, the iodine acts as network terminator and allows breaks in the continuity of the network structure. For low content of AgI, the Ag^+ diffusion does not significantly occur in the glass compared to the electron charge carriers. But beyond 15% mol. of AgI, the mobility of Ag^+ ions becomes dominating by means of conduction

pathways. From optical fiber point of view, the best candidate in $(\text{GeTe}_4)_{100-x}(\text{AgI})_x$ system is assumed to be $(\text{GeTe}_4)_{85}(\text{AgI})_{15}$ since it possesses the lowest electrical conductivity meaning the lowest optical losses once shaped into fibers.

Acknowledgments

Financial support from European Community's Seventh Framework Programme through Marie-Curie Action: “Initial Training Networks” (GlaCERCo GA 264526) is gratefully acknowledged. The authors are also very grateful to Prof. E. Bychkov and Prof. T. Usuki for useful discussions.

Reference

- [1] S. Cui, C. Boussard-Plédel, J. Lucas, B. Bureau, Te-based glass fiber for far-infrared biochemical sensing up to 16 μm , *Opt. Express*, 22 (2014) 21253-21262.
- [2] C. Conseil, J.-C. Bastien, C. Boussard-Plédel, X.-H. Zhang, P. Lucas, S. Dai, J. Lucas, B. Bureau, Te-based chalcogenide glasses for far-infrared optical fiber, *Opt. Mater. Express*, 2 (2012) 1470-1477.
- [3] N. Tohge, T. Minami, Y. Yamamoto, M. Tanaka, Electrical and optical properties of n-type semiconducting chalcogenide glasses in the system Ge-Bi-Se, *J. Appl. Phys.*, 51 (1980) 1048-1053.
- [4] M. Afifi, H. Labib, M. El-Fazary, M. Fadel, Electrical and thermal properties of chalcogenide glass system $\text{Se}_{75}\text{Ge}_{25-x}\text{Sb}_x$, *Appl. Phys. A*, 55 (1992) 167-169.
- [5] E. Bychkov, G. Wortmann, ^{121}Sb Mössbauer study of insulating and ion-conducting antimony chalcogenide-based glasses, *J. Non-Cryst. Solids*, 159 (1993) 162-172.
- [6] M. Kawasaki, J. Kawamura, Y. Nakamura, M. Aniya, Ionic conductivity of $\text{Ag}_x(\text{GeSe}_3)_{1-x}$ ($0 < x < 0.571$) glasses, *Solid State Ionics*, 123 (1999) 259-269.
- [7] R. Belin, G. Taillades, A. Pradel, M. Ribes, Ion dynamics in superionic chalcogenide glasses:: Complete conductivity spectra, *Solid State Ionics*, 136–137 (2000) 1025-1029.

- [8] P. Boolchand, W. Bresser, Mobile silver ions and glass formation in solid electrolytes, *Nature*, 410 (2001) 1070-1073.
- [9] M. Ureña, A. Piarristeguy, M. Fontana, B. Arcondo, Ionic conductivity (Ag^+) in AgGeSe glasses, *Solid State Ionics*, 176 (2005) 505-512.
- [10] I. Alekseev, M. Kassem, M. Fourmentin, D. Le Coq, R. Iizawa, T. Usuki, E. Bychkov, Ionic and electronic transport in AgI–As₂Te₃ glasses, *Solid State Ionics*, 253 (2013) 181-184.
- [11] Z. Li, C. Lin, G. Qu, L. Calvez, S. Dai, X. Zhang, T. Xu, Q. Nie, Formation and properties of chalcogenide glasses based on GeS₂–Sb₂S₃–AgI system, *Mater. Lett.*, 132 (2014) 203-205.
- [12] A.P. Gonçalves, E.B. Lopes, G. Delaizir, J.B. Vaney, B. Lenoir, A. Piarristeguy, A. Pradel, J. Monnier, P. Ochin, C. Godart, Semiconducting glasses: A new class of thermoelectric materials?, *J. Solid State Chem.*, 193 (2012) 26-30.
- [13] P. Lucas, C. Conseil, Z. Yang, Q. Hao, S. Cui, C. Boussard-Pledel, B. Bureau, F. Gascoin, C. Caillaud, O. Gulbiten, T. Guizouarn, P. Baruah, Q. Li, J. Lucas, Thermoelectric bulk glasses based on the Cu-As-Te-Se system, *J. Mater. Chem. A*, 1 (2013) 8917-8925.
- [14] J.B. Vaney, A. Piarristeguy, A. Pradel, E. Alleno, B. Lenoir, C. Candolfi, A. Dauscher, A.P. Gonçalves, E.B. Lopes, G. Delaizir, J. Monnier, M. Ribes, C. Godart, Thermal stability and thermoelectric properties of Cu_xAs_{40-x}Te_{60-y}Se_y semiconducting glasses, *J. Solid State Chem.*, 203 (2013) 212-217.
- [15] M. Sekine, Y. Suzuki, H. Ueno, Y. Onodera, T. Usuki, T. Nasu, S. Wei, Appearance of fast ionic conduction in AgI-doped chalcogenide glass powders prepared by mechanical milling, *J. Non-Cryst. Solids*, 353 (2007) 2069-2073.
- [16] T. Minami, Fast ion conducting glasses, *J. Non-Cryst. Solids*, 73 (1985) 273-284.
- [17] H.L. Tuller, M. Barsoum, Glass solid electrolytes: Past, present and near future—the year 2004, *J. Non-Cryst. Solids*, 73 (1985) 331-350.
- [18] M. Tatsumisago, T. Saito, T. Minami, Fabrication of mesoscopic composites composed of α -AgI and AgI-based superionic glass, *Thermochimica acta*, 280 (1996) 333-341.

- [19] T. Usuki, S. Saito, K. Nakajima, O. Uemura, Y. Kameda, T. Kamiyama, M. Sakurai, Structural and electrical properties of AgI dispersed As-chalcogenide glasses, *J. Non-Cryst. Solids*, 312 (2002) 570-574.
- [20] H.W. Sun, B. Tanguy, J.-M. Reau, J.J. Videau, J. Portiek, Investigations on glasses in the Sb_2S_3 -AgI system, *J. Non-Cryst. Solids*, 99 (1988) 222-232.
- [21] J. Ren, Q. Yan, T. Wagner, V. Zima, M. Frumar, B. Frumarova, G. Chen, Conductivity study on GeS_2 - Ga_2S_3 -AgI-Ag chalcogenide glasses, *J. Appl. Phys.*, 114 (2013) 023701.
- [22] M. Kassem, D. Le Coq, M. Bokova, E. Bychkov, Chemical and structural origin of conductivity changes in CdSe -AgI- As_2Se_3 glasses, *Solid State Ionics*, 181 (2010) 466-472.
- [23] I. Alekseev, M. Kassem, D. Le Coq, M. Bokova, M. Fourmentin, E. Bychkov, $^{110\text{m}}\text{Ag}$ tracer diffusion studies of CdSe -AgI- As_2Se_3 glasses, *Solid State Ionics*, 181 (2010) 1467-1472.
- [24] C. Tubandt, E. Lorenz, *Nernst's Festschrift*, W. Knapp, Halle (Saale), 1912.
- [25] K. Ramesh, S. Asokan, K. Sangunni, E. Gopal, Electrical Switching in germanium telluride glasses doped with Cu and Ag, *Appl. Phys. A*, 69 (1999) 421-425.
- [26] G. Sreevidya Varma, C. Das, S. Asokan, Evidence of an intermediate phase in a quaternary Ag bearing telluride glass system using alternating DSC, *Solid State Commun.*, 177 (2014) 108-112.
- [27] Y.G. Vlasov, E. Bychkov, Ion-selective chalcogenide glass electrodes, *Ion-Selective Electrode Rev*, 9 (1987) 5-93.
- [28] E. Bychkov, M. Elidrissi Moubtassim, J. Jumas, Ionic transport crossover in mixed conducting chalcogenide glasses detected by ^{125}Te -Mössbauer spectroscopy, *J. Non-Cryst. Solids*, 260 (1999) 180-187.
- [29] Y.V. Bobylev, E. Bychkov, Y.S. Tver'yanovich, Electrical properties of glasses in the AgI- As_2Te_3 system, *Glass Phys. Chem*, 30 (2004) 519-522.
- [30] S. Stehlik, J. Kolar, M. Bartos, M. Vlcek, M. Frumar, V. Zima, T. Wagner, Conductivity in Ag-As-S (Se, Te) chalcogenide glasses, *Solid State Ionics*, 181 (2010) 1625-1630.

- [31] H.W. Sun, B. Tanguy, J.-M. Reau, J.-J. Videau, J. Portier, P. Hagenmuller, Physical and chemical characterization and ionic conductivity of rapidly quenched glasses in the $\text{Sb}_2\text{S}_3\text{Ag}_2\text{SAgI}$ system, *J. Solid State Chem.*, 70 (1987) 141-150.
- [32] A. Ganjoo, R. Golovchak, Computer program PARAV for calculating optical constants of thin films and bulk materials, *J. Optoelectron. Adv. Mater.*, 10 (2008) 1328-1332.
- [33] M. Sakurai, F. Kakinuma, E. Matsubara, K. Suzuki, Partial structure analysis of amorphous $\text{Ge}_{15}\text{Te}_{80}\text{M}_5$ (M= Cu, Ag and In), *J. Non-Cryst. Solids*, 312 (2002) 585-588.
- [34] A.A. Wilhelm, C. Boussard-Plédel, Q. Coulombier, J. Lucas, B. Bureau, P. Lucas, Development of Far-Infrared-Transmitting Te Based Glasses Suitable for Carbon Dioxide Detection and Space Optics, *Adv. Mater.*, 19 (2007) 3796-3800.
- [35] Z. Yang, P. Lucas, Tellurium Based Far Infrared Transmitting Glasses, *J. Am. Ceram. Soc.*, 92 (2009) 2920-2923.
- [36] T.-C. Wen, W.-C. Chen, Gelled composite electrolyte comprising thermoplastic polyurethane and poly (ethylene oxide) for lithium batteries, *J. Power Sources*, 92 (2001) 139-148.
- [37] Z. Borisova, *Glassy semiconductors*, Plenum, New York, 1981.
- [38] A. Giridhar, S. Mahadevan, Silver as a dopant and as a constituent in As-Ag-Te glasses: electrical conductivity, *J. Non-Cryst. Solids*, 197 (1996) 228-234.
- [39] C. Julien, G. Nazri, *Solid State Batteries: Materials Design and Optimization: Materials Design and Optimization*, Kluwer academic publishers, London, 1994.
- [40] C. Moynihan, D. Gavin, R. Syed, Pre-exponential term in the Arrhenius equation for electrical conductivity of glass, *Le Journal de Physique Colloques*, 43 (1982) C9-395-C399-398.
- [41] A. Pradel, M. Ribes, Ion transport in superionic conducting glasses, *J. Non-Cryst. Solids*, 172 (1994) 1315-1323.
- [42] E. Bychkov, V. Tsegelnik, Y. Vlasov, A. Pradel, M. Ribes, Percolation transition in Ag-doped germanium chalcogenide-based glasses: conductivity and silver diffusion results, *J. Non-Cryst. Solids*, 208 (1996) 1-20.

- [43] A. Pradel, N. Kuwata, M. Ribes, Ion transport and structure in chalcogenide glasses, *J. Phys.: Condens. Matter*, 15 (2003) S1561.
- [44] P. Jónvári, S. Cui, V. Nazabal, I. Kaban, B. Beuneu, M. Dussauze, C. Boussard - Plédel, B. Bureau, Network Rearrangement in AgI - Doped GeTe₄ Glasses, *J. Am. Ceram. Soc.*, (2014).
- [45] V. Nguyen, J. Sanghera, J. Freitas, I. Aggarwal, I. Lloyd, Structural investigation of chalcogenide and chalcohalide glasses using Raman spectroscopy, *J. Non-Cryst. Solids*, 248 (1999) 103-114.
- [46] X. Wang, Q. Nie, G. Wang, J. Sun, B. Song, S. Dai, X. Zhang, B. Bureau, C. Boussard, C. Conseil, H. Ma, Investigations of Ge–Te–AgI chalcogenide glass for far-infrared application, *Spectrochim. Acta, Part A*, 86 (2012) 586-589.
- [47] P. Lucas, Z. Yang, M.K. Fah, T. Luo, S. Jiang, C. Boussard-Plédel, M.-L. Anne, B. Bureau, Telluride glasses for far infrared photonic applications, *Opt. Mater. Express*, 3 (2013) 1049-1058.
- [48] P. Lucas, C. Boussard-Plédel, A. Wilhelm, S. Danto, X.-H. Zhang, P. Houizot, S. Maurugeon, C. Conseil, B. Bureau, The Development of Advanced Optical Fibers for Long-Wave Infrared Transmission, *Fibers*, 1 (2013) 110-118.

Figure captions

Fig. 1. DC electrical conductivities of Ag- (red squares), I- (blue triangles) and AgI-based (black circles) GeTe_4 glasses following the Ag or I or AgI content. The measurements were performed by four probe system at room temperature ($T = 293\text{K}$). The dotted lines are given as a guide for eyes.

Fig. 2. (a) Nyquist's plot of the glass TG-AgI20 at different temperatures; temperature dependence on the AC electrical conductivities of $(\text{GeTe}_4)_{100-x}\text{Ag}_x$ glasses (b), $(\text{GeTe}_4)_{100-x}(\text{AgI})_x$ glasses with $x \leq 15$ mol. % (c), and $(\text{GeTe}_4)_{100-x}(\text{AgI})_x$ glasses with $x > 15$ mol. % (d)

Fig. 3. Tauc plots of $(\text{GeTe}_4)_{100-x}\text{Ag}_x$ (a) and $(\text{GeTe}_4)_{100-x}(\text{AgI})_x$ (b) glasses versus photon energy.

Fig. 4. Evolution of the two types of conductivity measured at 293K in the Ag- (red symbols) and AgI- (black symbols) based glasses following the Ag or AgI content. The dotted lines for AC measurements are given as a guide for eyes.

Fig. 5. Nyquist's plot of $(\text{GeTe}_4)_{100-x}(\text{AgI})_x$ glasses at 293 K for $0 \leq x \leq 25$ highlighting the appearance of the polarization arm for high AgI contents.

Fig. 6. (a) Activation energy E_a and (b) pre-exponential factor σ_0 of $(\text{GeTe}_4)_{100-x}(\text{AgI})_x$ and $(\text{GeTe}_4)_{100-x}\text{Ag}_x$ glasses vs. Ag or AgI content.

Fig. 7. Structural model of $(\text{GeTe}_4)_{100-x}\text{Ag}_x$ (a) and $(\text{GeTe}_4)_{100-x}(\text{AgI})_x$ (b) glasses

Table

Table 1 Glass transition temperature (Tg), electrical conductivities σ_{AC} and σ_{DC} , optical band gap E_{opt} , pre-exponential factor σ_0 , and activation energy E_a of $(\text{GeTe}_4)_{100-x}(\text{AgI})_x$ and $(\text{GeTe}_4)_{100-x}\text{Ag}_x$ glasses (T = 293K). Uncertainties on the last digit(s) are given in the brackets.

Sample	Composition [mol.%]	T g ($^{\circ}$ C)	Log ₁₀ σ_{AC} [S·cm ⁻¹]	Log ₁₀ σ_{DC} [S·cm ⁻¹]	E_{opt} [eV]	E_a [eV]	Log ₁₀ σ_0 [S·cm ⁻¹]
TG-AgI0	GeTe ₄	15 7(2)	- 5.02(18)	- 5.20(10)	0.6 5(1)	0.453 (9)	5.25 (18)
TG-AgI5	(GeTe ₄) ₉₅ (AgI) ₅	14 8(2)	- 5.53(14)	- 5.74(10)	0.7 0(1)	0.478 (14)	5.14 (14)
TG-AgI10	(GeTe ₄) ₉₀ (AgI) ₁₀	14 6(2)	- 6.02(12)	- 6.29(10)	0.7 5(1)	0.515 (7)	5.32 (12)
TG-AgI12.5	(GeTe ₄) _{87.5} (AgI) _{12.5}	14 4(2)	- 6.17(4)	- 6.44(10)	0.7 8(1)	0.525 (3)	5.19 (4)
TG-AgI15	(GeTe ₄) ₈₅ (AgI) ₁₅	14 3(2)	- 6.38(13)	- 6.56(10)	0.8 0(1)	0.532 (16)	5.25 (13)
TG-AgI17.5	(GeTe ₄) _{82.5} (AgI) _{17.5}	14 1(2)	- 6.02(4)	- --	0.8 3(1)	0.469 (3)	4.52 (4)
TG-AgI20	(GeTe ₄) ₈₀ (AgI) ₂₀	14 0(2)	- 5.50(7)	- --	0.8 4(1)	0.414 (4)	4.09 (7)
TG-AgI25	(GeTe ₄) ₇₅ (AgI) ₂₅	13 5(2)	- 4.48(20)	- --	0.9 0(1)	0.278 (3)	3.16 (20)
TG-Ag0	GeTe ₄	15 7(2)	- 5.02(18)	- 5.20(10)	0.6 5(1)	0.453 (9)	5.25 (18)
TG-Ag5	(GeTe ₄) ₉₅ Ag ₅	14 6(2)	- 4.80(12)	- 5.00(10)	0.6 0(1)	0.453 (6)	5.46 (12)
TG-Ag10	(GeTe ₄) ₉₀ Ag ₁₀	14 8(2)	- 4.44(3)	- 4.63(10)	0.5 8(1)	0.433 (2)	5.52 (3)
TG-Ag15	(GeTe ₄) ₈₅ Ag ₁₅	14 8(2)	- 4.15(3)	- 4.25(10)	0.5 7(1)	0.412 (2)	5.42 (3)
TG-Ag20	(GeTe ₄) ₈₀ Ag ₂₀	15 0(2)	- 4.00(5)	- 4.04(10)	0.5 7(1)	0.374 (3)	4.92 (5)

Figure 1

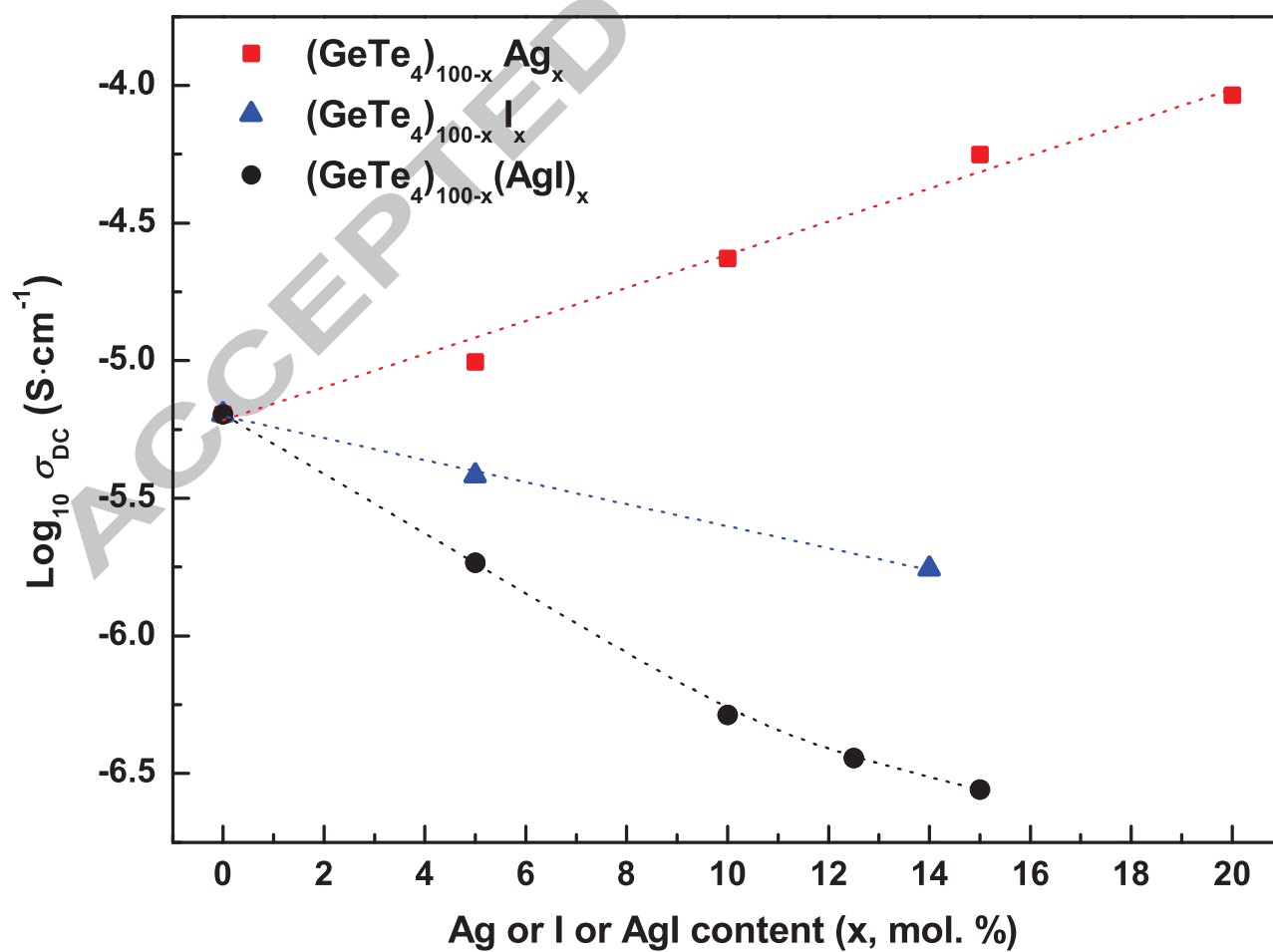


Figure 2

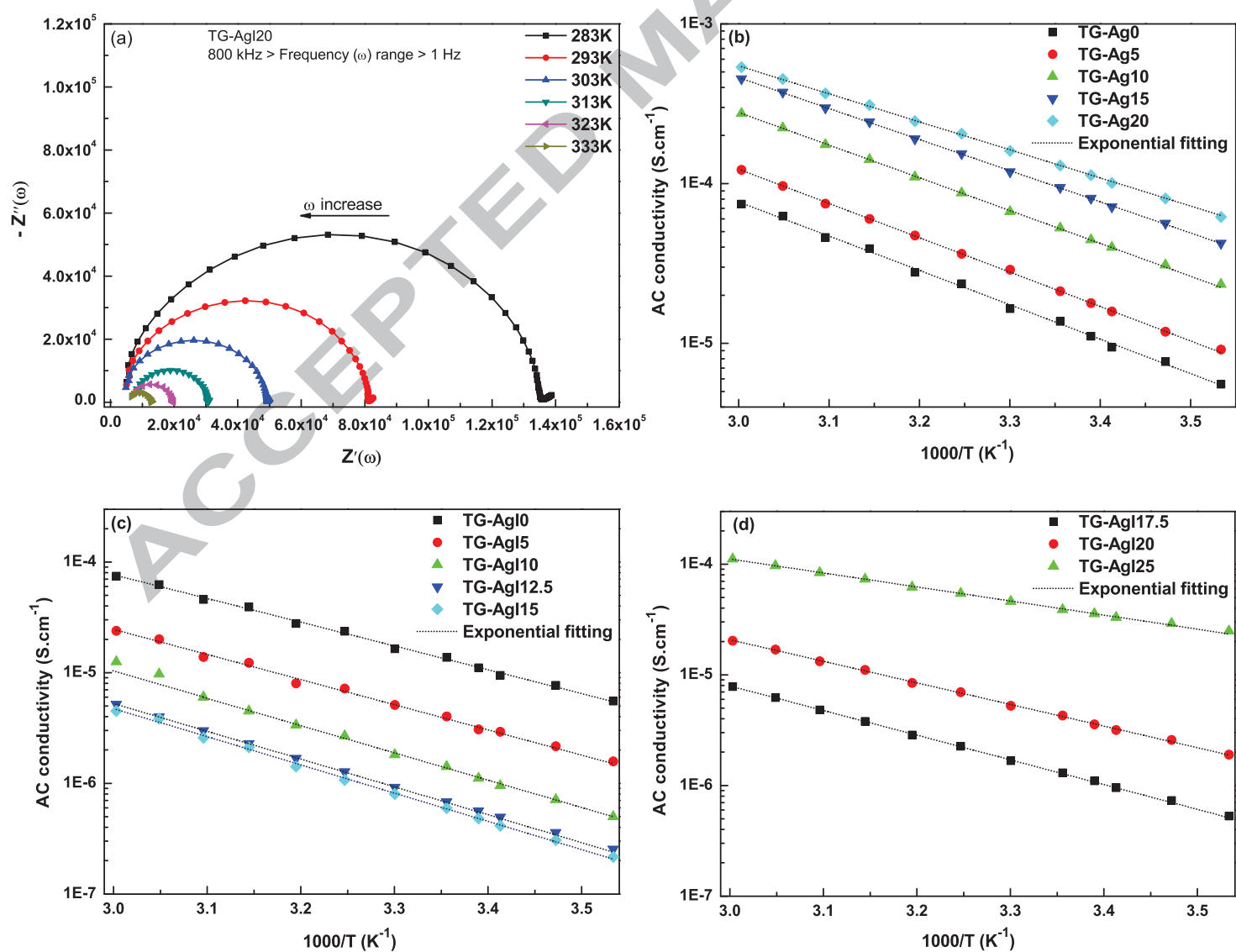


Figure 3

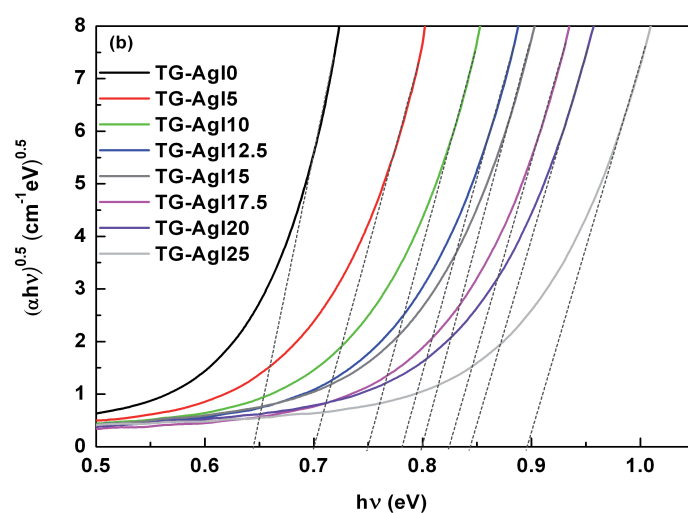
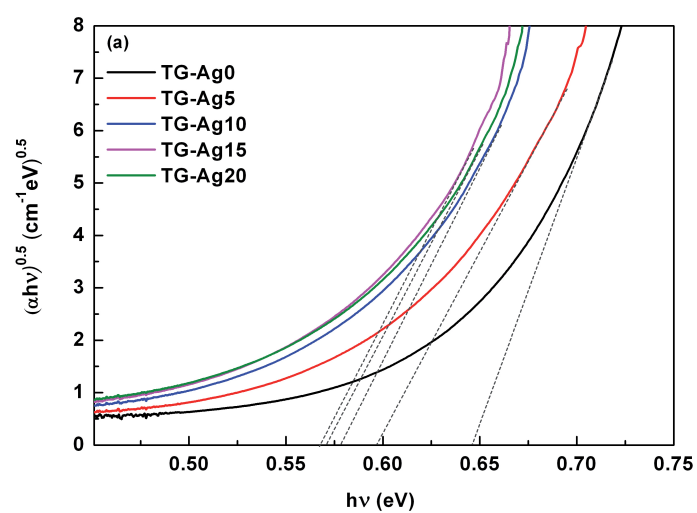


Figure 4

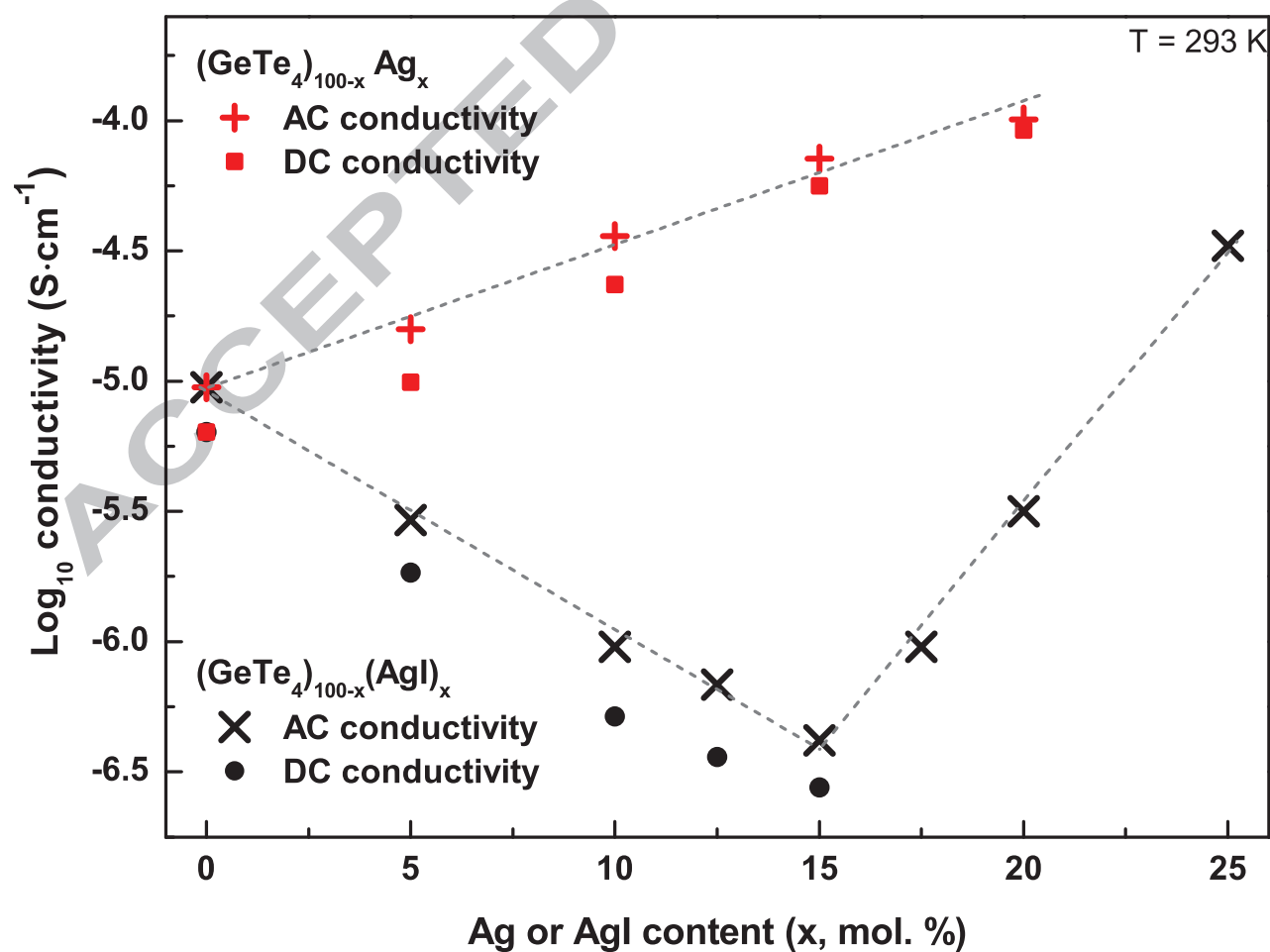


Figure 5

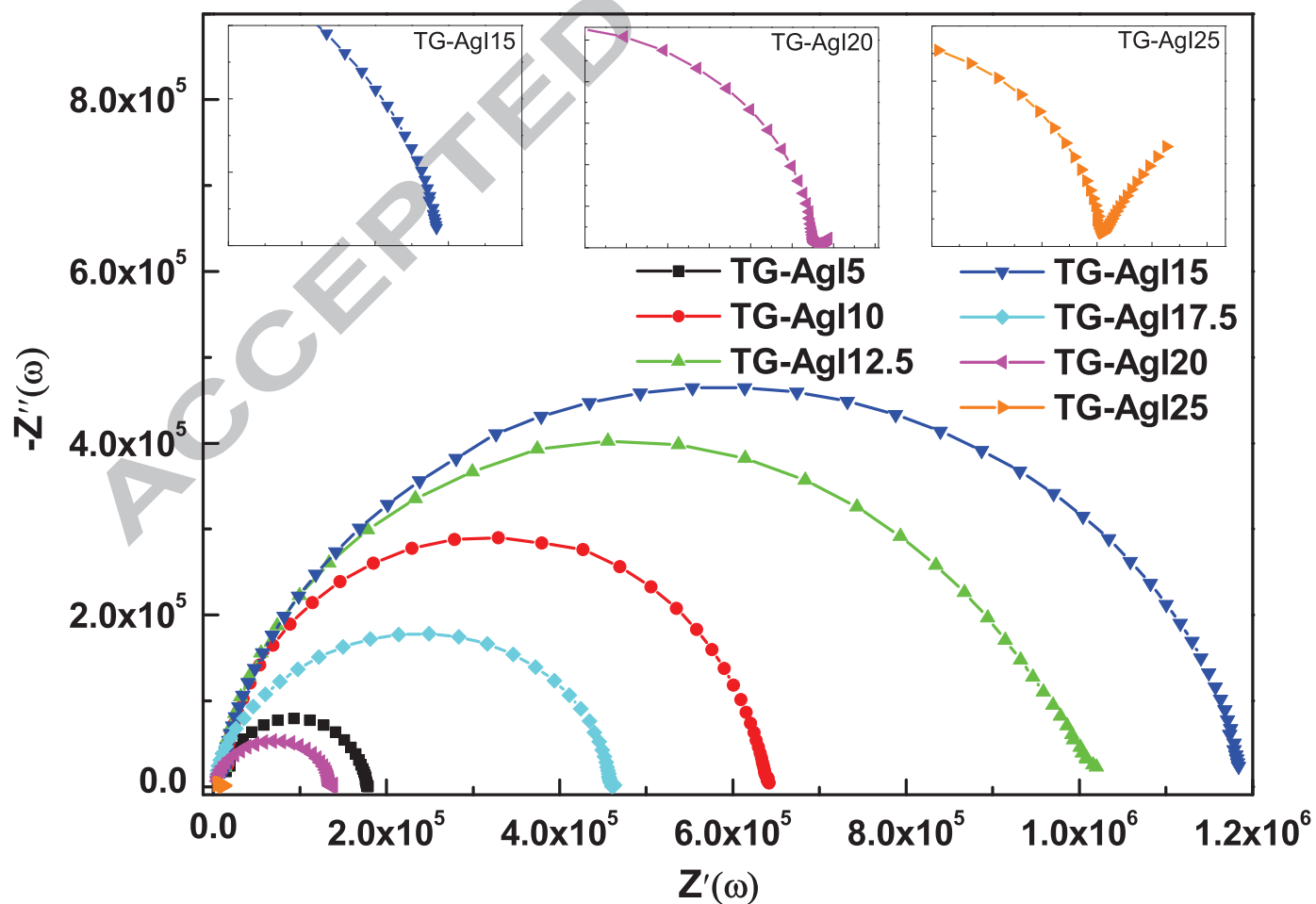
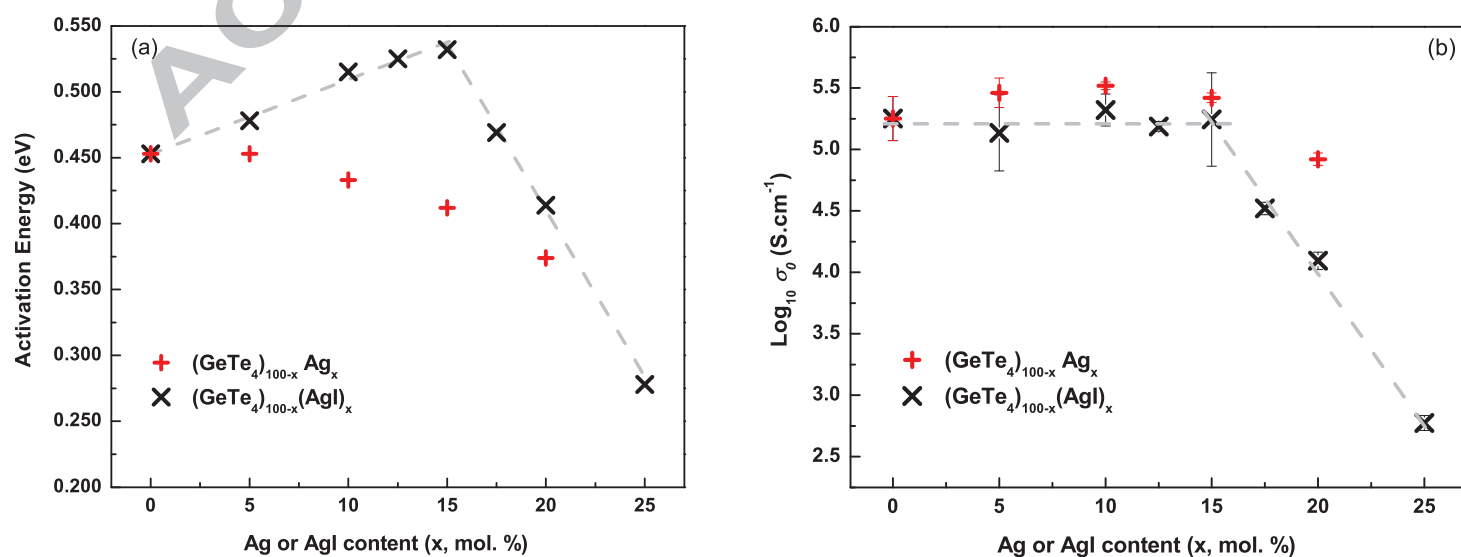
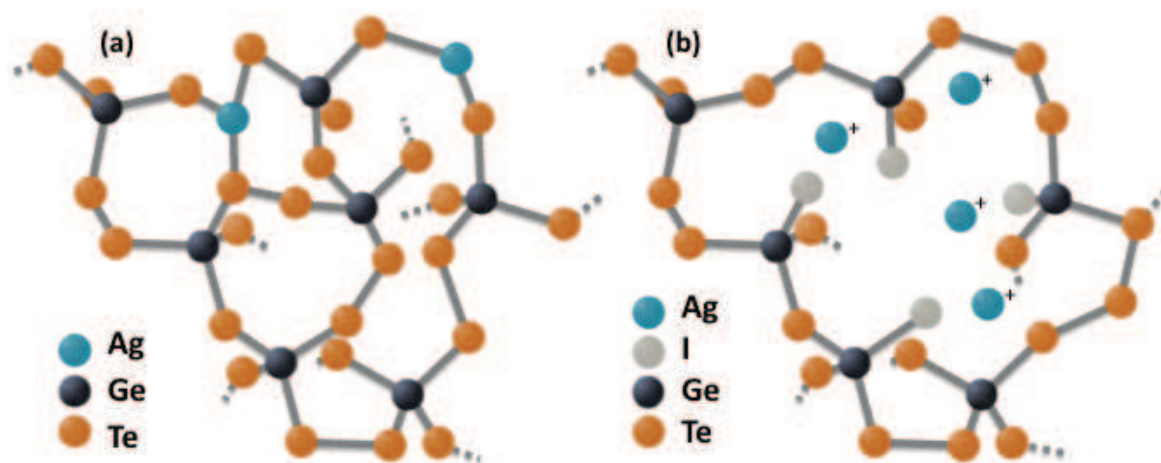
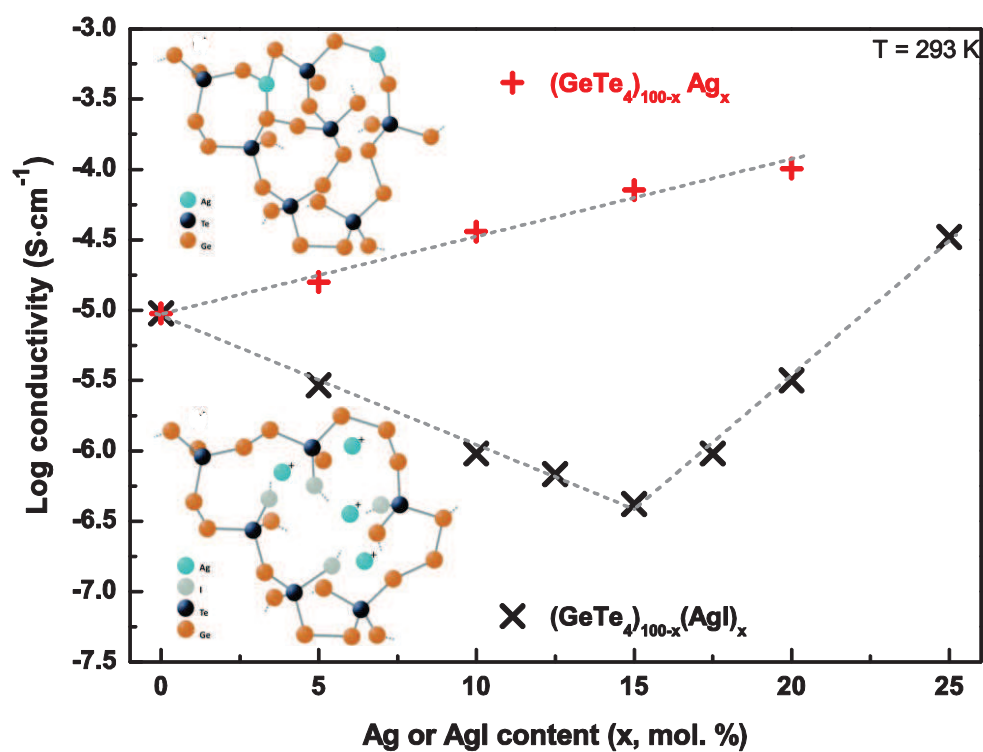


Figure 6







Highlights

- Evolution of the electrical conductivities in Ag- and AgI- GeTe_4 glasses
- We demonstrate a change of a conductivity type (electronic vs ionic) in AgI- GeTe_4 glasses
- A structural model for Ag- and AgI- GeTe_4 glasses is proposed
- The role of Ag in the structure of the Ag- and AgI- GeTe_4 glasses is described